

Electron-Phonon Interactions in Polyacene Organic Transistors

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We present a simple model for the electron-phonon interactions between the energy subbands in polyacene field-effect transistors and the vibrations of the crystal. We introduce a generalized Su-Schrieffer-Heeger model, arguing that the strongest electron-phonon interactions in these systems originate from the dependence of inter-molecule hopping amplitudes on collective molecular motion. We compute the electron-phonon spectral function $\alpha^2 F(\omega)$ as a function of two-dimensional hole density and the coupling strength constant. Our results are in agreement with the sharp onset of superconductivity near half-filling discovered in recent experiments by Schön *et al.* [1] and predict an increase of T_c with pressure. We further speculate on the implications that the observation of the quantum Hall effect in these systems has on the effective band mass in the low carrier density regime.

Present studies [1,2] of high-mobility organic transistors by Batlogg and collaborators have shown an immense richness of tunability of their electronic properties with gate voltage of in a single device. New possibilities for studying the physics of coherent *band* quasiparticle transport in organic semiconductors have been open by the high quality of these organic single crystals and of their interfaces with AlO_3 dielectrics. To date, however, the analysis of organic field-effect-transistor electronic systems has been hampered by the absence of simple and reliable models for their electronic quasiparticles and for the interactions of these quasiparticles with each other and with vibrations of the host lattice. Indeed the discovery of coherent band quasiparticle properties and of the quantum Hall effect in these systems, which are usually thought of as being complex and relatively disordered, has been one of the major surprises that has emerged from recent materials quality advances.

At temperatures above $\approx 20\text{K}$ the transport electronic properties of polyacene semiconductors are well described by *small polaron* theory [3]. However, this small polaron theory is based on localized molecular orbitals and is therefore unable to describe the low-temperature *band* quasiparticle behavior seen in Battlogg *et al.*'s samples. Schubnikov-de Haas transport measurements in these samples demonstrate a quasiparticle mean-free-paths in excess of 1000 lattice constants, demonstrating that the low-temperature regime can be described only by starting at the opposite limit and building a theory based on delocalized band quasiparticles states. Nevertheless, the interactions of quasiparticles with lattice vibrations remain strong, and are presumably responsible for superconductivity. We propose a simple tight-binding model for the quasiparticle bands originating from the π -molecular orbitals and for the interaction of these bands with the host crystal vibrational excitations. Our theory is parameter free once the band mass has been specified [2].

We focus, for simplicity, on the polyacene compound anthracene, which is monoclinic ($P2_1/a$) with two basis molecules whose orientations are related by a glide

ing plane symmetry. We start by considering the field-induced energy bands obtained neglecting electron-phonon interactions. The key question we need to address is the number of 2D subbands that are occupied at a particular 2D density, n_{2D} . We find that all carriers reside in a single subband up to much higher density in these transistors than in their inorganic counterparts, principally because of the relatively small dielectric constants ($\epsilon \sim 3.5$) and the large effective in plane band mass ($m_{\perp} = 1.5m_e$) and in spite of the rather large c-direction effective band mass $m_z \sim 3m_e$ [1]. Our conclusion is based partially on envelope-function density-functional calculations for which the local-density-approximation (LDA) can be used to estimate many-body effects [4] that favor a single subband. In our LDA calculations we find that the second subband is first populated at $n_{2D} \approx 5 - 7 \times 10^{14}\text{cm}^{-2}$, a density just larger than the highest achieved in experimental systems. Since the experimental signatures of second subband occupation would be unambiguous and no anomalies in 2D density dependence have been reported, we conclude that a single 2D subband is occupied up to the highest densities and that the lowest subband is strongly localized in the top layer for n_{2D} larger than $\approx 10^{13}\text{cm}^{-2}$.

Because Huckel model intra-molecular hopping parameters have no linear dependence on low energy intra-molecular vibration normal coordinates, our model Hamiltonian includes only inter-molecular hopping parameters [5]. Then to model the electron-phonon interaction, we expand each $a - b$ plane hopping parameter to first order in the twelve coordinates that describe rigid rotations and displacements of neighboring polyacene molecules (as it is usually done in the Su-Schrieffer-Heeger model [6]):

$$t = t_0 + \sum_{m=1}^6 \sum_{\mu} \tilde{t}_{\mu,m} \tilde{u}_{\mu,m} \quad (1)$$

where $\tilde{u}_{\mu,m}$ is the generalized displacement coordinate, $\mu = 1, 2$ is the molecular basis index, $m = 1, 2, 3$ de-

note displacements of the molecular center of mass along \hat{x}, \hat{y} and \hat{z} directions, and $m = 4, 5, 6$ denote angular displacements around the 1, 2, 3 principal axes angular displacements around the 1, 2, 3 principal axes of each molecule. The electron-phonon interaction parameters $\tilde{t}_{\mu,m} \equiv \partial t / \partial \tilde{u}_{\mu,m}$ are calculated based on the assumption of proportionality between hopping integrals and overlap integrals between HOMO or LUMO orbitals on adjacent molecules. These are calculated using standard Hückel approximation HOMO π orbitals and hence appropriate to the hole systems on which we focus.

We next present expressions for the interactions terms in the Hamiltonian between phonons of the host crystal and the 2D band quasiparticles. The phonon frequencies and polarization vectors are obtained by solving the standard secular equation involving the dynamical matrix. These eigenmodes are in general a mixture of displacements and rotations. We compute the dynamical matrix following the procedure outlined in Ref. [7]. The phonon density-of-states and dispersion curves that emerge from these calculations have been reported elsewhere and are omitted here for the sake of brevity [8]. The rigid-molecule vibration approximation used here is a convenient but inessential approximation that can be complemented if necessary by including coupling to important isolated molecule vibrations; it is however reasonably accurate for low-frequency vibrations of anthracene becoming less reliable for larger polyacenes.

Combining these ingredients we finally write the Hamiltonian (ignoring the Coulomb interaction term) as $\mathcal{H} = \mathcal{H}_{2D}^0 + \mathcal{H}_{2D\text{-vib}} + \mathcal{H}_{\text{vib}}$, where

$$\mathcal{H}_{2D\text{-vib}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in \text{BZ}} \sum_{\nu \alpha \beta, i, j} \sum_{\mathbf{Q} \in \text{BZ}} g_{i, \alpha; j, \beta}(\mathbf{k}, \mathbf{Q}, \nu) \times [\hat{a}_{\mathbf{Q}, \nu} + \hat{a}_{-\mathbf{Q}, \nu}^\dagger] \hat{c}_{i, \alpha[\mathbf{k}+\mathbf{Q}]}^\dagger \hat{c}_{j, \beta \mathbf{k}} \quad (2)$$

and

$$g_{i, \alpha; j, \beta}(\mathbf{k}, \mathbf{q}, q_z, \nu) = (-1)^i \frac{\tilde{f}_{\alpha, \beta}(q_z)}{2} \sum_{\tilde{\delta}', \mu, m} \sqrt{\frac{\hbar}{2\tilde{M}_{\mu, m} \omega_\nu(\mathbf{Q})}} \times \tilde{t}_{\mu m}(\tilde{\delta}') \epsilon_{\mu m}(\mathbf{Q}, \nu) e^{i\mathbf{q} \cdot \tilde{\delta}_\mu} (e^{-i\tilde{\delta}' \cdot [\mathbf{k}+\mathbf{q}]} + (-1)^{(i-j)} e^{i\tilde{\delta}' \cdot \mathbf{k}}). \quad (3)$$

In Eq. 3 $\tilde{f}_{\alpha, \beta}(q_z) = \sum_{z_l} a_l^{\alpha*} a_l^\beta e^{iq_z z_l}$ is the form factor of the subband (indexed by i, j) tight-binding wave function and the brackets indicate reduction to the 2D BZ. In our calculations we use the strict 2D limit ($\tilde{f}_{\alpha, \beta}(q_z) = 1$) because of the strong quantum confinement found in LDA and Hartree calculations.

We next define the electron-phonon interaction spectral function as

$$\alpha^2 F(\omega) \equiv \frac{1}{N g(\mu)} \sum_{\mathbf{k}, \mathbf{k}', i} \sum_{q_z, \nu} |g_{i, 1; i, 1}(\mathbf{k}, [\mathbf{k}' - \mathbf{k}], q_z, \nu)|^2 \times \delta(\epsilon_i(\mathbf{k}) - \mu) \delta(\epsilon_i(\mathbf{k}') - \mu) \delta(\omega - \omega_\nu([\mathbf{k}' - \mathbf{k}], q_z)) \quad (4)$$

where $g(\mu) = \sum_{\mathbf{k}} \delta(\epsilon_i(\mathbf{k}) - \mu)$ is the electronic density of states, and $[\mathbf{k}' - \mathbf{k}]$ denotes the projection of the $\mathbf{Q} = (\mathbf{k}' - \mathbf{k}, q_z)$ vector into the three dimensional BZ. The results of these calculations for densities $n_{2d} = 4.0 \times 10^{14} \text{ cm}^{-2}$, $n_{2D} = 1.4 \times 10^{14} \text{ cm}^{-2}$, and $n_{2D} = 6.7 \times 10^{13} \text{ cm}^{-2}$ are shown in Fig. 1. The peak locations in the low-frequency rigid molecule vibration regime agree with those observed in infrared absorption and tunneling data in pentacene crystals [2]. The mass enhancement factor λ , obtained from the integration of $2F\alpha^2(\omega)/\omega$, close to half filling is 0.25. Its sharp decay away from half-filling (driven by the density of states) helps explain the sharp superconductivity onset observed in the experiments, and as a consequence we expect a suppression of superconductivity beyond half-filling from this simple theory. We estimate the superconducting critical temperature by the [dimension independent] BCS expression $k_B T_c \approx \hbar \omega_D \exp[-1/\lambda]$. Such expression, using $\hbar \omega_D / k_B \approx 150 \text{ K}$ from Ref. [2], yields $\sim 3 \text{ K}$ in agreement with the experiments [1]. We note that the inclusion of the second-nearest-neighbour hopping tends to push the density of states peak to higher energies (densities). Adding a finite life time of the quasiparticles, will broaden these peaks, hence creating a plateau in the n_{2D} -dependence of T_c shifted to the right of half filling as observed in the experiments [1]. This last effect would lower also the T_c calculated at $n = 4.00 \times 10^{12} \text{ cm}^{-2}$, worsening experimental agreement. However, given that E_F does not satisfy $E_F \gg \hbar \omega_{max}$, such estimates of T_c from λ must be considered qualitative.

In summary we have presented a theory of the low-temperature quasiparticle bands in polyacene field effect transistors, and of the electron-phonon coupling with the host molecular crystal. Our calculations indicate that the quasiparticles lie in a single 2D tight-binding band up to the highest densities that have been achieved experimentally at present and that the most important electron-phonon interactions arise from the influence of approximately rigid molecular translations and rotations on hopping between HOMO and LUMO orbitals on adjacent molecules. This picture implies a dependence of superconducting critical temperature on molecular lattice constant which contrasts with the case of doped fullerene superconductors. For the fullerenes, the important electron-phonon interactions are intra-molecular so that T_c depends on inter-molecular hopping only through the density-of-states. Decreasing the lattice constant, increases hopping, and hence decreases the density-of-states and T_c [9]. Here decreasing the lattice constant will also strengthen the important electron-phonon interactions. According to our theory, the latter effect dominates and T_c will increase with decreasing lattice constant. We find that phonon-mediated electron-electron interactions in polyacene molecular crystals are strong only when the 2D tight-binding band is close to half-filling and its density of states is relatively large. This oc-

curs for 2D densities comparable to $4 \times 10^{14} \text{cm}^{-2}$, where superconductivity turns on relatively abruptly. At lower carrier densities, $\lambda \ll 1$ and electron-electron interactions are dominated by repulsive Coulomb interactions, consistent with the occurrence of the fractional quantum Hall effect. We also note that the simple fact that the fractional quantum Hall effect is observed points to the distinct possibility that the band mass can be highly reduced at those lower carrier densities since, otherwise, from rough estimates of the known experimental values at higher carrier densities, the r_s value would be too large to allow anything but a Wigner crystal ground state.

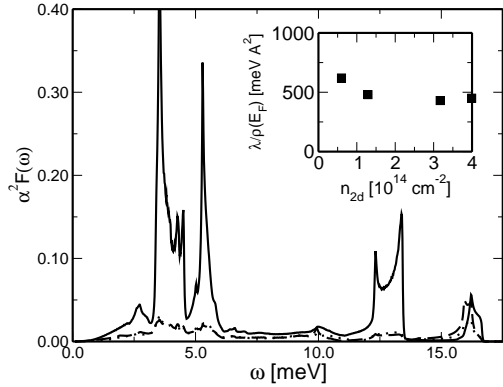


FIG. 1. $\alpha^2 F(\omega)$ for $n_{2d} = 4.0 \times 10^{14} \text{cm}^{-2}$ (solid line), $n_{2d} = 1.4 \times 10^{14} \text{cm}^{-2}$ (dotted line), and $n_{2d} = 6.7 \times 10^{13} \text{cm}^{-2}$ (dashed line).

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